

The First Stable Lower Fullerene : C₃₆

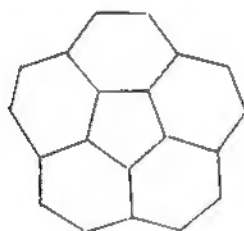
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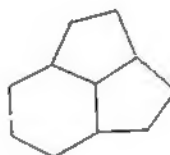
A new pure carbon material, presumably composed of thirty six carbon atom molecules, has been synthesized and isolated in milligram quantities¹. It appears as though these molecules have a closed cage structure making them the smallest member of a new class of molecules known as fullerenes, most notably of which is the soccer ball shaped C₆₀². However, unlike other known fullerenes, any closed, fullerene-like C₃₆ cage will necessarily contain fused pentagon rings³. Therefore, this molecule apparently violates the isolated pentagon rule, a criterion which requires isolated pentagons for stability in fullerene molecules^{4,5}. Striking parallels between this problem and the synthesis of other fused five member fused ring systems will be discussed. Also, it will be shown that certain biological structures known as clathrin behave in a manner which gives excellent predictions about fullerenes and nanotubes. These predictions help to explain the presence of abundant quantities of C₃₆ in arced graphite soot.

Fused Pentagon Fullerenes

The discovery of Buckminsterfullerene (C₆₀) demonstrated the possibility of producing graphite-like molecular structures by bending the planar sp² carbon bonds of graphite⁷. Although such strained ring systems are common to organic chemists, "buckyballs" are unique only in that the carbon structure closes on itself requiring no passivation of bonds by hydrogen. In fact, it is useful to think of the C₆₀ molecule as a continuation of the C₂₀H₁₀, corannulene unit (I) which has the structure of a central pentagon surrounded by fused hexagons (one third of a C₆₀ molecule)⁶. Prior to the discovery of C₆₀, one could have inferred this molecule's stability based on the existence of corannulene which possesses comparable strain and curvature of the sp² carbon bonds.



I.



II.

This method of applying information about previously synthesized fused ring systems to the problems of novel fullerenes may also be addressed to fullerenes with fused pentagons such as C₃₆. The first logical step in this progression is to pose the question of whether or not fused cyclopentano ring systems exist in organic chemistry literature. Indeed, such species have been synthesized and the first of these fused pentagon ring systems was 2,2a,3,4-tetrahydro-1H-cyclopent[cd]indene (II). This molecule falls into a class of 5,5,6 fused ring molecules which various groups had attempted to synthesize from the mid-1920's through the early 1950's⁸. The failure of this effort to yield any conclusive results lead some chemists to speculate that such a strained ring system may not be stable enough to exist. However, in 1956, Rapoport & Pasky developed an effective method of

CP442, *Electronic Properties of Novel Materials: XII International Winterschool*
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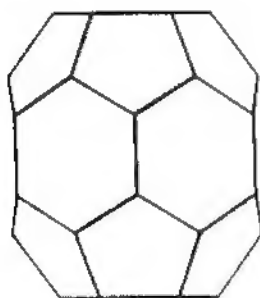
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synthesizing and characterizing II⁸. It was concluded that the fused pentagon ring system is not as highly strained as previously believed.

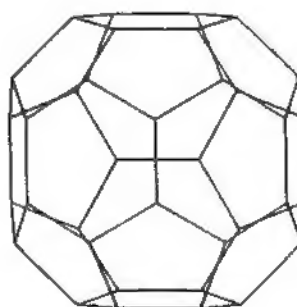
Similarly, the lack of evidence of lower fullerenes in crude fullerene mass spectra has lead some to speculate that fused pentagon fullerenes cannot exist outside of vapor phase mass spectrometry experiments^{4,5}. On the contrary, we have found that C₃₆ is stable in solid form. Our findings, the details of which are reported elsewhere¹, indicate that the chemistry of this new fullerene is significantly different from other known fullerenes. For example, C₃₆ is insoluble in the common "fullerene" solvents such as toluene or benzene. However, we have found that it is soluble in pyridine, a fact which has aided tremendously in the bulk synthesis. Also, laser desorption mass spectrometry of pristine C₃₆ is difficult due to the fact that the molecule is easily destroyed by the laser pulse. One way to remedy this problem has been to use a matrix such as the fullerene soot in which C₃₆ is generated. Alternatively, somewhat more robust derivatives such as C₃₆H₆ have been synthesized and successfully tested by mass spectrometry. We speculate that the combination of such factors may have prevented the discovery of this material until now.

Clathrin

Perhaps one of the most striking analogs to fullerenes is that of the clathrin protein which is found in various types of animal cells^{6,9,10}. Clathrin is a long, rigid molecule having a molecular weight of about 180,000 a.m.u.. It is observed to link together into a hexagonal, graphite-like network on the surface of vesicles. Although this is the most preferred orientation, clathrin is known to form pentagons in order to enclose a tubular or spherical vesicle. Much can be learned from the types of structures which result, especially when applied to closed graphitic structures such as fullerenes and nanotubes. For example, clathrin coats on micro tubules possess various chiralities and diameters similar to those observed in single-walled and multi-walled nanotubes. Also, large, spherical particles were first observed to have an icosahedral, soccer ball shaped clathrin coat, like C₆₀. One might expect that any closed structure consisting of pentagons and hexagons would form but that is not the case. For example, Of the higher fullerenes analogs, only the C₈₂ isomers with isolated pentagons have been observed in abundance⁶.



III.



IV.

Therefore, it appears intuitive to study the structures observed for lower fullerene clathrin analogs. Given that there are over five hundred lower fullerene-like, clathrin structures possible³, only four have been observed. Two of these structures are analogs of C₃₆ isomers. One with D_{6h} symmetry (III) and one with D_{2d} symmetry (IV)^{6,10}. Amazingly, recent calculations on the fifteen possible isomers of C₃₆ have predicted these exact structures to be lowest in energy as well as isoenergetic¹¹. Clathrin must have to obey the same rules of minimizing strain by distributing curvature evenly over the entire structure. Not surprisingly, our experimental results strongly suggest that the C₃₆ samples synthesized contain the D_{6h} isomer in abundance¹.

Conclusion

To our knowledge, the isolation of C₃₆ signifies the first successful bulk synthesis of a lower fullerene. We have found that although the molecule is stable, various factors such as heightened sensitivity to photochemical degradation as well as low solubility has prevented synthesis of this material in the past. The fact that isolated pentagons is not an absolute requirement for stability has been discussed. Also, parallels have been drawn to the protein clathrin which coats vesicles in a graphite-like network. Strong evidence has been presented that this material is constrained upon closure in ways which are very similar to fullerenes. This appears to make clathrin an excellent model for predicting which fullerenes should be expected.

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References

1. C. Piskoti, J. Yarger, A. Zettl, Submitted to Nature
2. See, for example, *Buckminsterfullerenes*, W. Edward Billups and Marco A. Ciufolini, (VCH Publishers, New York, 1993)
3. P. W. Fowler, & D. E. Manolopoulos, *An Atlas of Fullerenes* (Clarendon Press, Oxford, 1995).
4. H. W. Kroto, Nature **329**, 529-531 (1987)
5. R. E. Smalley, *Accts. Chem. Res.* **25**, 98-105 (1992)
6. D. Koruga, et. al., *Fullerene C₆₀* (Elsevier Science Publishers, North-Holland, 1993)
7. R. C. Haddon, *Accts. Chem. Res.* **21**, 243-249 (1988)
8. H. Rapoport & J. Z. Pasky, *J. Amer. Chem. Soc.* **78**, 3788-3792 (1956)
9. T. Kanaseki & K. Kadota, *J. Cell Biol.* **42**, 202-220 (1969)
10. R. A. Crowther, J. T. Finch and B. M. F. Pearse, *J. Mol. Biol.* **103**, 785-798 (1976)
11. J. C. Grossman, M. Côté, S. G. Louie & M. L. Cohen, *Chem. Phys. Lett.* **284**, 344-349 (1998).